Electrochemical degradation of PAH compounds in process water

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Electrochemical degradation of PAH compounds in process water

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Introduction

PAHs (Polycyclic Aromatic Hydrocarbons)

Main sources
- Burning of fossil fuels (oil and coal)
- Wood stove heating of houses and cigarette smoke
- Tar production and use

Human health effects
- Highly toxic, carcinogenic, mutagenic

Threshold values (drinking water)
- 0.005 - 0.010 µg L^{-1}

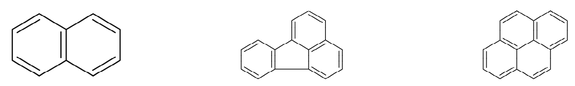
Characteristics
- Lipophilic and hence low water solubility
- Primarily found in soil and sediment
- Persistent, recalcitrant, and non-reactive

Objectives

- Determine the reaction kinetics for electrooxidation of PAHs in low concentration
- Evaluate the current efficiency at different experimental settings
- Proof the concept by treatment of process water from sediment purification

Experimental procedure

Model compounds



Naphthalene Fluoranthene Pyrene

Analytical technique
- HPLC-FLU (Fluorescence)
- Genuine triple determination

Batch recirculation setup

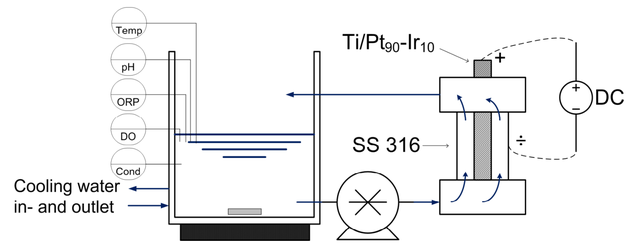


Figure 1: The investigation has been performed in a batch recirculation experimental setup at constant temperature with a commercial Watersafe cell of tubular design with Ti/Pt_{90}-Ir_{10} anode and SS 316 cathode operated at galvanostatic conditions. The volume of water in each run was 3 L with a constant recirculation flow of 430 L h^{-1}. Initial concentrations of the sum of PAHs were 6-10 mgL^{-1}. The three investigated electrolytes were Na_2SO_4, $NaNO_3$, and NaCl, the concentration range was 0.60-1.40 M, and the current densities were 15-200 mA cm^{-2}.

Results & discussion

Model solution study

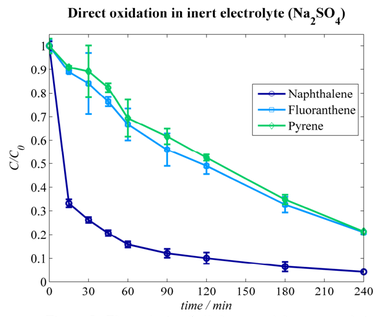


Figure 2: Electrolysis of all three model compounds in 0.10 M Na_2SO_4 at 200 mA cm^{-2}. All three PAHs are oxidized by direct anodic oxidation. However, a clear difference in the degradation curves is observed with a rapid initial oxidation of the two-ring structured naphthalene . The degradation curves do not correspond to full mineralization, but reflect the opening of a ring and loss of the fluorescent property.

The direct electrooxidation of naphthalene is faster than fluoranthene and pyrene (fig. 2)

The rates of oxidation are increased in a NaCl electrolyte and decreased in $NaNO_3$ (fig. 3)

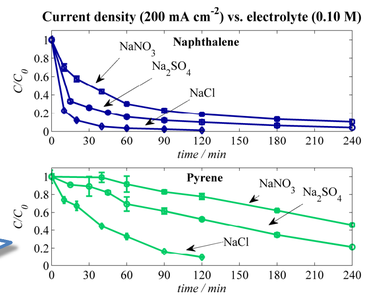


Figure 3: Electrolysis in different electrolytes at constant molar concentration and current density of 200 mA cm^{-2}. The rate of oxidation was significantly increased in NaCl due to indirect hypochlorous acid / hypochlorite oxidation.

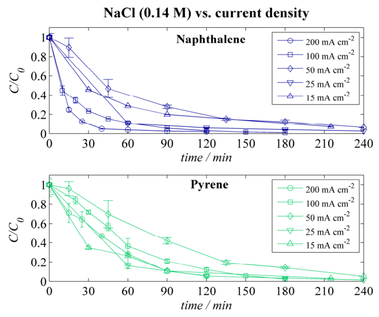


Figure 4: Electrolysis at different current densities in 0.14 M NaCl electrolytes. The observed trend is increased rate of oxidation at increased current density as expected. However, the degradation curves obtained at 15 and 25 mA cm^{-2} suggested a more current efficient PAH oxidation at these corresponding lower potentials.

The rates of oxidation are increased with increased current densities (fig. 4)

The rates of oxidation are decreased by reduced NaCl electrolyte concentration (fig. 5)

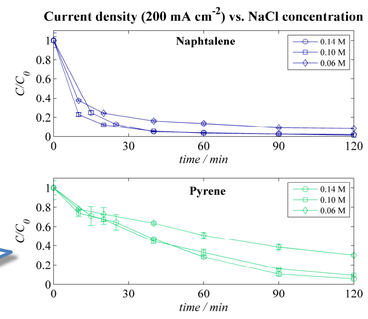


Figure 5: Electrolysis at constant current density of 200 mA cm^{-2} in different concentrations of NaCl electrolyte. The observed trend is decreased rate of oxidation when the concentration of chloride is lowered, clearly showing the importance of the indirect hypochlorous acid / hypochlorite oxidation in the degradation of the PAHs.

Process water study

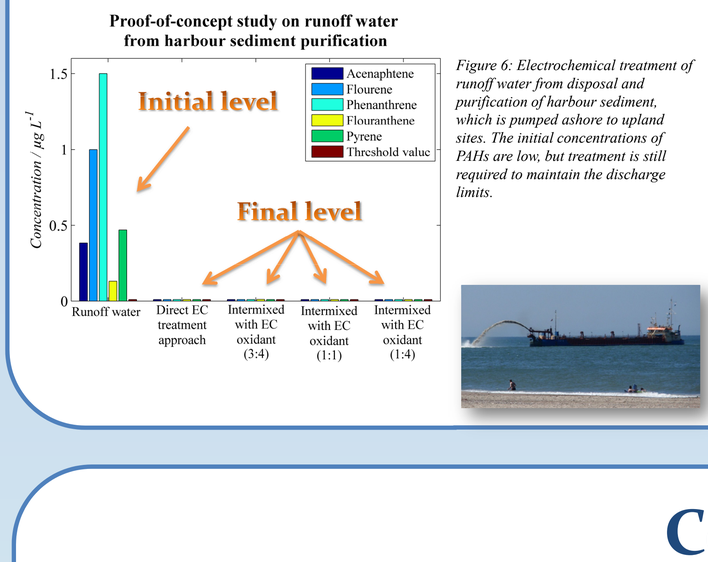


Figure 6: Electrochemical treatment of runoff water from disposal and purification of harbour sediment, which is pumped ashore to upland sites. The initial concentrations of PAHs are low, but treatment is still required to maintain the discharge limits.

Process water: Runoff water (salinity 1 $^{w}/_{w}$%) from disposal of contaminated harbour sediment (Water-sediment ratio is 5:1).

1. Approach: Batch recirculation treatment of 20 L in the setup (fig. 1) for 4 h at 200 mA cm^{-2}.

2. Approach: Intermixing in different ratios with electrochemically produced oxidant solution. 2 $^{w}/_{w}$% NaCl solution electrolyzed for 30 min to generate 2 g L^{-1} of free chlorine. Analyzed after 1 h.

Result: The final concentration in all four experiments maintained the threshold value of 0.010 µg L^{-1} (fig. 6).

Reaction kinetics

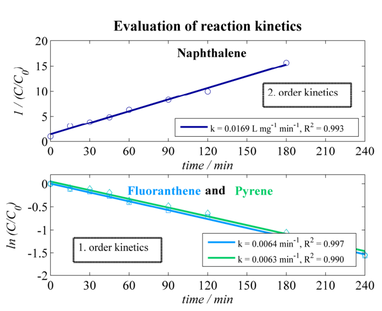


Figure 7: Evaluation of the observed reaction kinetics at 20 C. Under all investigated parameters naphthalene followed 2. order kinetics whereas fluoranthene and pyrene followed 1. order kinetics. The example showed in this figure is the evaluation of the degradation curves in figure 2.

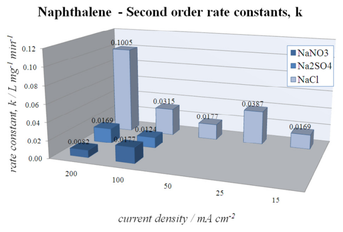
Naphthalene:
The electrochemical oxidation followed under all investigated parameters **2. order** reaction kinetics.

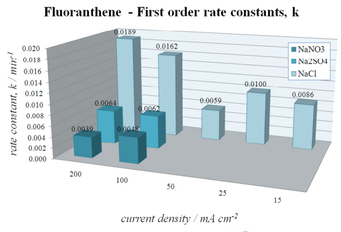
$$\frac{d[Naphthalene]}{dt} = -k \cdot [Naphthalene]^2$$

Fluoranthene and Pyrene:
The degradation curves could be sufficiently modeled to standard **1. order** reaction kinetics.

$$\frac{d[Fluoranthene]}{dt} = -k \cdot [Fluoranthene] \qquad \frac{d[Pyrene]}{dt} = -k \cdot [Pyrene]$$

Rate constants





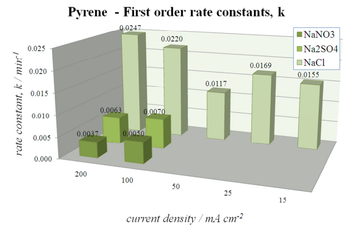


Figure 8: The rate constants for the oxidation of naphthalene, fluoranthene and pyrene obtained by the different experimental settings. The fastest reaction rates are clearly obtained in the NaCl electrolyte independent of reaction kinetics.

Direct oxidation mechanisms (Simplified):

$$M + H_2O \rightarrow M[OH^{\bullet}] + H^+ + e^- \rightarrow MO + 2H^+ + 2e^- \Rightarrow \quad M[OH^{\bullet}] + R \rightarrow M + ROH + e^-$$

$$MO + R \rightarrow M + RO$$

Indirect oxidation mechanisms (Simplified):

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \rightleftharpoons OCl^- + Cl^- + 2H^+ \Rightarrow \quad OCl^- + R \rightarrow RO + Cl^-$$

$$HOCl + R \rightarrow RO + Cl^- + H^+$$

Current efficiency

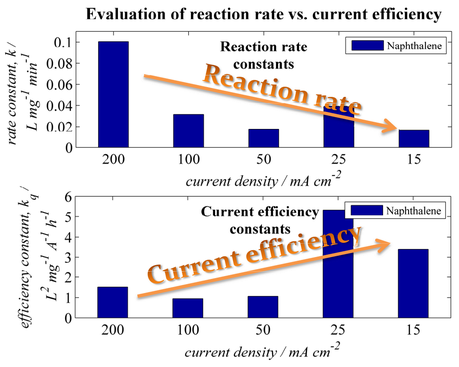


Figure 9: Comparison of reaction rates and current efficiencies with naphthalene as an example. As the current density was decreased, the reaction rate went down, but the current efficiency went up. It means that at the low current densities, a higher yield of PAH degradation was obtained per spent ampere (cost), but the necessary reaction time was higher (reactor size).

When the evolution in PAH concentration at different current densities is evaluated with respect to the specific amount of charge passed through the solution, Q (Ah L^{-1}), a current efficiency constant, k_q, can be defined similar to the rate constant:

$$\frac{d[Naphthalene]}{dQ} = -k_q \cdot [Naphthalene]^2$$

As figure 9 shows, the current efficiency (electrons in the circuit arising from naphthalene oxidation) is increased, when the current density is decreased.

This is believed to be caused by suppression of the unwanted water oxidation side reaction at the lower applied potentials.

Conclusion

- Naphthalene, fluoranthene, and pyrene in low concentrations were efficiently degraded by electrochemical oxidation in the batch recirculation setup
- The degradation were significantly enhanced in NaCl electrolyte by the indirect hypochlorous acid / hypochlorite oxidation
- The oxidation of naphthalene followed 2. order reaction kinetics, whereas fluoranthene and pyrene followed 1. order kinetics
- The current efficiencies of the oxidation were increased at low current densities

Acknowledgements

Ministry of Science Technology and Innovation

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